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NRL Report 4487

**A METALLURGICAL EVALUATION
OF REFRACTORY COMPOUNDS
CONTAINING MOLTEN TITANIUM**

PART II - CARBON, GRAPHITE, AND CARBIDES

E. J. Chapin and W. H. Friete

**Nonferrous Alloys Branch
Metallurgy Division**

December 15, 1954



**NAVAL RESEARCH LABORATORY
Washington, D.C.**

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The names of the manufacturers from whom the experimental crucibles and materials were obtained have been coded in compliance with NRL policy. Inquiries should be addressed to NRL Code 6310. The information contained herein shall not be used for advertising purposes.

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ABSTRACT

Crucibles of high purity carbon with exceptionally smooth dense surfaces and of commercially pure and spectroscopically pure graphite were investigated to determine if purity and surface finish were beneficial factors. The results were negative.

The monocarbides of Ti, Zr, V, Nb, Ta, and W were investigated for their suitability as crucible materials for melting titanium. All the carbides were attacked by molten titanium resulting in general solution of the crucible and contamination of the melt, principally with carbon. TiC was found to be the main carbide phase occurring in the metal, derived from reduction of the crucible carbide by molten titanium at the liquid-solid interface. The carbides are not considered suitable crucible materials.

PROBLEM STATUS

This report completes the investigation of carbon, graphite, and carbide materials for use in melting of titanium.

AUTHORIZATION

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A METALLURGICAL EVALUATION OF REFRACTORY COMPOUNDS FOR CONTAINING MOLTEN TITANIUM PART II - CARBON, GRAPHITE, AND CARBIDES

INTRODUCTION

The essential requirements for melting titanium in a refractory crucible and the results of an investigation of various oxides as crucible materials were presented in the Part I report of this series (1). Part II presents the results of the investigation of melting titanium in crucibles of graphite, of carbon, and of various carbides.

Carbon and graphite are used extensively for crucibles and for furnace linings. Both surpass all other refractory materials in resistance against softening under load at temperatures up to 2000°C. Graphite melts at about 3800°C, while pure carbon has no melting point but sublimates at 3450°C. Commercial investigation of melting titanium in graphite crucibles demonstrated that graphite lacked adequate inertness. The metal generally was contaminated with sufficient carbon to affect adversely its mechanical properties. Therefore, no extensive evaluation of graphite or carbon crucibles was planned. It was believed desirable, however, to determine if high purity was a beneficial factor. High-purity commercial graphite and a spectroscopically pure grade were selected for study. In addition, a pure carbon as derived from a reaction between an organic compound (furfural) and an acid (2) was also selected, not only from purity considerations but also because of its unique manner of agglomeration into a binder-free solid.

A survey of materials with desirable refractory qualities (Part I) showed that the transition metals of the fourth, fifth, and sixth groups of the periodic table form carbides (3-9) having characteristics that offered possibilities for their consideration for refractory purposes. These compounds are characterized by bonds of high energy as evidenced by their large heats of formation, high melting points, and extreme hardness. Other reported properties include chemical inertness and high mechanical strength at elevated temperatures. The stability of the carbides at high temperatures, based on thermodynamic considerations (8,9), appeared sufficiently attractive to warrant their consideration as possible crucible materials for melting titanium. The monocarbides of Ti, Zr, Nb, V, Ta, and W were selected for investigation since these were the most stable and had optimum properties.

Crucibles of the above mentioned materials were obtained as follows: those of graphite were machined from source-H bar stock; those of microcrystalline pure carbon were cast in glass molds by reacting acid with furfural; those of the various carbides were obtained from source E and were hot pressed in graphite at 2000°C.

Inasmuch as the experimental details were previously described in Part I, only a brief account of the procedure used for the evaluation of the graphite, carbon, and carbide crucibles is presented. Melts made

in carbon and graphite crucibles were heated in a high-frequency induction vacuum furnace and permitted to solidify in the crucible. Melts made in carbide crucibles were heated in a molybdenum furnace designed for tilt pouring and fitted with a tungsten wire heater, using vacuum or helium atmosphere. In certain instances single melts were solidified in the crucible to study interface conditions. In all cases, repeated melts were made in order to study the effects of melting on the crucible and the metal separately.

INVESTIGATION OF CARBON AND GRAPHITE

The organic compound, furfural when reacted with HCl, results in the precipitation of carbon which agglomerates into a solid mass by forming a skeletal structure. When this reaction is conducted against highly polished glass mold surfaces the resulting carbon casting accommodates itself to these surfaces producing comparable surfaces at the interface. It was found that firing these castings at temperatures above 900°C in vacuum resulted in the surfaces acquiring a very dense, smooth, and lustrous finish. Small crucibles of 1/2-in. bore by 7/8-in. o.d. by 2 in. high, were prepared in this manner.

After outgassing one of these crucibles at 1380°C in vacuum, a melt was attempted with a 4-gram titanium charge to test the resistance of the crucible. Inspection showed that the crucible bore was wetted by the molten titanium but was apparently otherwise unaffected. Then a second charge of 16 grams of titanium was added to the 4-gram melt; a second melt was made and solidified in the crucible. Melting occurred quietly with no visible reaction. Subsequent examination of the crucible revealed a pronounced wetting of the crucible bore extending over the top of the crucible and down the outside for about 1/4 in.; the wetting appeared to replace the dense lustrous surface of the carbon with a bright metallic coating.

Microstructural examination of the melt revealed serious carbon contamination (Fig. 1A). An interface layer of titanium carbide was formed between the carbon crucible and molten titanium. This layer, however, did not provide an effective barrier against solution of approximately 3.5% carbon into the melt. This high carbon content is reflected by the amount of the TiC phase present in the microstructure (Fig. 1A). Hardness measurements showed an average of about 225 DPH for the metallic matrix and about 800 DPH for the carbide phase. No further attempts were made to melt titanium in this material.

A melt consisting of a 25-gram titanium charge was attempted in a crucible of 3/4-in. bore by 1-1/4-in. o.d. by 3 in. high machined from high-purity commercial graphite. Melting proceeded quietly without any apparent reaction; however, upon subsequent examination it was found that the metal had reacted locally with the graphite and soaked through the crucible as illustrated in Fig. 1B. The bright areas appearing on the crucible show zones of crucible penetration



Fig. 1A - Carbon crucible (furfural) melt showing TiC interface layer and carbides, unetched, 25X



Fig. 1C - Spectroscopically pure graphite crucible melt showing TiC interface layer and carbides, unetched, 50X.

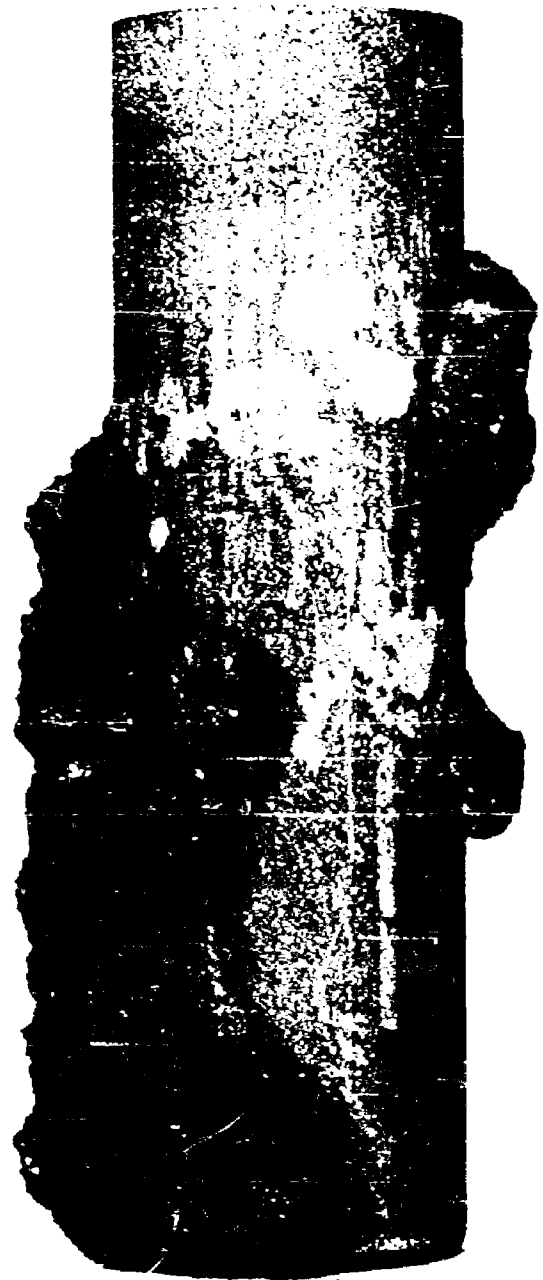


Fig. 1B - High purity commercial graphite crucible showing penetration by molten metal; full size.

by molten metal. It is believed that the porosity of the graphite was partially responsible for the melt being completely drained from the crucible. A melt was attempted in another crucible of the same grade of graphite which had a 1/4-in. diam. hole at the apex of a conical bottom to permit draining of the melt. However, this melt did not drain through the hole, but reacted locally with the graphite and soaked through the crucible. Investigation of this material was discontinued after these unsuccessful attempts.

A melt consisting of an 18-gram charge was attempted in vacuum in an outgassed crucible 3/4-in. bore by 1-in. o.d. by 3 in. high machined from spectroscopically pure graphite. The molten metal soaked through the crucible. A second charge of 16 grams of titanium was melted in this same crucible in an attempt to develop a carbide interface layer that might serve as a possible inhibiting barrier between the crucible and the molten metal. Inspection of the crucible after the second melting showed that some of the second melt had solidified in the crucible without appreciable soaking. A third charge of about 14 grams of titanium was added, melted, and allowed to solidify in the crucible. The resulting well-defined interface layer of titanium carbide and the heavy carbide contamination of the melt are shown in Fig. 1C. Hardness of the interface layer was found to average about 1129 DPH, while the metallic matrix containing the carbides averaged about 430 DPH.

It was demonstrated by these experiments that the factor of high purity in either carbon or graphite crucibles did not prove beneficial. Furthermore, the dense, smooth surfaces obtained in the carbon crucibles cast from the furfural-acid reaction, were of no value in inhibiting reaction with molten titanium. Titanium carbide interface layers did not prove effective in preventing extensive solution of carbon into the melt. In view of these discouraging results further evaluation of carbon and graphite materials was discontinued.

INVESTIGATION OF CARBIDES

The monocarbides of Ti, Zr, V, Nb, Ta, and W, selected for investigation, are metallic in character and have thermal and electrical conductivity in the order of magnitude of pure metals, a positive temperature coefficient of resistivity, high hardness values, a high modulus of elasticity, high melting points; and correspondingly high strength at elevated temperatures. The thermodynamic properties and the relative nonvolatility in vacuum at the melting point of titanium indicate high-temperature chemical stability. The properties of these carbides are listed in Table 1.

The monocarbides of Ti, Zr, V, Nb, and Ta have a common structure of NaCl type, and are reported to be isomorphous and soluble in one another (10-13). Tungsten monocarbide has a simple hexagonal structure and high solubility in TiC. The various

TABLE I
Characteristic Properties of Selected Refractory Carbides

Carbide	Density (g/cc)	Crystal Habit	Carbon Range (wt%)	Resistivity (microhms/cm at 20°C)	Thermal Conductivity (cal/cm sec°C)	- ΔF_{298} (Kcal/g atom of carbon)	Melting Point (°C)
TiC	4.25	NaCl	6.5 to 20	193	0.041	56.2	3140
ZrC	6.90	NaCl	10.0 to 11.64	63.4	0.049	42.0	3175
VC	5.36	NaCl	19.08	156		27.5	2830
NbC	7.82	NaCl	8.85 to 11.45	147	0.034	18.7	3500
TaC	14.48	NaCl	5.5 to 6.23	30	0.053	8.6	3800
WC	15.5	Hex	6.13	53		3.9	2630

monocarbides apparently are able to exist in a range of carbon contents without change in phase (Table 1). TiC has the widest range from about 6.5 to 20 wt% while VC barely reaches the required stoichiometric amount. The solubility of oxygen and nitrogen in the carbides of the fourth and fifth groups of the periodic table generally prevents the achievement of stoichiometric carbon content, the vacant lattice positions being readily filled by oxygen or nitrogen. TiC appears to have the highest free energy of formation of any of the carbides listed in Table 1. This indicates that molten titanium may reduce the carbides below it to form TiC.

The carbides selected for investigation were processed into crucibles by hot pressing in graphite at temperatures of at least 2000°C in order to obtain maximum density. Chemical analyses of the crucible carbides for combined carbon, free carbon, oxygen, nitrogen, and hydrogen together with corresponding X-ray diffraction data are tabulated in Table 2. It was found that with the exception of VC the crucible carbides showed a carbon content close to the theoretical amount representing saturation. No free carbon was found chemically in any of the crucible carbides while oxygen and nitrogen were exceptionally low except in the case of the nitrogen content in TiC. A qualitative spectrochemical check for other impurities revealed that no significant amounts were present. The lattice parameter values obtained are in close agreement with the best published values showing that the crucible carbides were relatively pure materials.

Melting was observed to proceed quietly in all of the carbide crucibles with no detectable vapor evolution. All of the melts were difficult to pour at the temperatures employed, exhibiting poor fluidity and becoming viscous shortly after complete melting was achieved. In all of the melting experiments molten titanium was observed to climb and wet the entire bore of the crucible before the charge was completely molten. Attempts to introduce a solid metal charge into a crucible heated to a high temperature always resulted in the metal sticking to the crucible upon the slightest contact. The experimental results are summarized in Table 3.

All of the crucibles displayed good thermal shock resistance and no cracking was observed during melting or after pouring. Crucibles were cracked when melts were intentionally solidified in them.

The pronounced wetting of the various crucible carbides by molten titanium is demonstrated by the deep meniscuses and their acute angle of contact with the crucible walls and also by the metal coatings on the crucible walls (Figs. 2A, 2B, 2C, 2D, 3A, 3B, 3C, 3D). This characteristic is indicative of a high surface energy and of a high reactivity of the carbides and molten titanium, and explains the seizure of the solid metal charge upon contact with the heated carbide crucible. Undercutting of the carbide wall by the melt at the top of the various meniscuses (Figs. 2A, 2C, 2D, 3A) is evidence of the solvent action of molten titanium on the carbides.

TABLE 2
Chemical and X-Ray Diffraction Analyses of Carbide Crucibles

Crucible Carbide	Chemical Analysis			X-Ray Diffraction Analysis			
	Carbon (%)	Found*	Oxygen (%)	Nitrogen (%)	Hydrogen (%)	Phases Found	Crystal Structure
	Possible Range						Lattice Parameter (Å)
							Crucible Carbide Literature
TiC	6.5 to 20	19.15	0.28	1.13	0.0050	TiC (ratio 1:1)	F.C.C. 4.3253 a_0 4.33
ZrC	10.0 to 11.64	11.80	0.24	0.268	0.0050	ZrC, some impurities, but not ZrO ₂ , ZrN, or Zr	F.C.C. 4.6942 a_0 4.69
VC	19.08	17.43	0.018	0.276	0.0022	VC, some impurities, but not V, VN, V ₂ O ₃ or V ₂ O ₅	F.C.C. 4.1688 a_0 4.15
NbC	8.85 to 11.45	11.36	0.029	0.122	0.0020	NbC, some impurities, possibly NbN or Nb	F.C.C. 4.4731 a_0 4.45
TaC	5.5 to 6.23	6.23	0.011	0.026	0.0007	TaC, some impurities including Ta ₂ O ₅	F.C.C. 4.4554 a_0 4.44
WC	6.13	6.00	0.010	0.067	0.0014	WC, some impurities including W, Fe but not W ₄ O ₁₁ , WO ₂ , WO ₃ , W ₂ C, WN	Hex 2.9076 a_0 2.90 2.8433 c_0 2.83 0.9779 c/a 0.975

*No free carbon detected



Fig. 2A - TaC crucible melt showing undercutting, general solution attack and some penetration by molten Ti; 2X, melt no. RM-50.



Fig. 2B - TiC crucible melt showing undercutting and general solution attack by molten Ti; 2X, melt no. RM-49.

Fig. 2C - ZrC crucible melt showing wetting characteristics of molten Ti; 2X, melt no. RM-55.



Fig. 2D - VC crucible melt showing undercutting and general solution attack by molten Ti; 2X, melt no. RM-46.



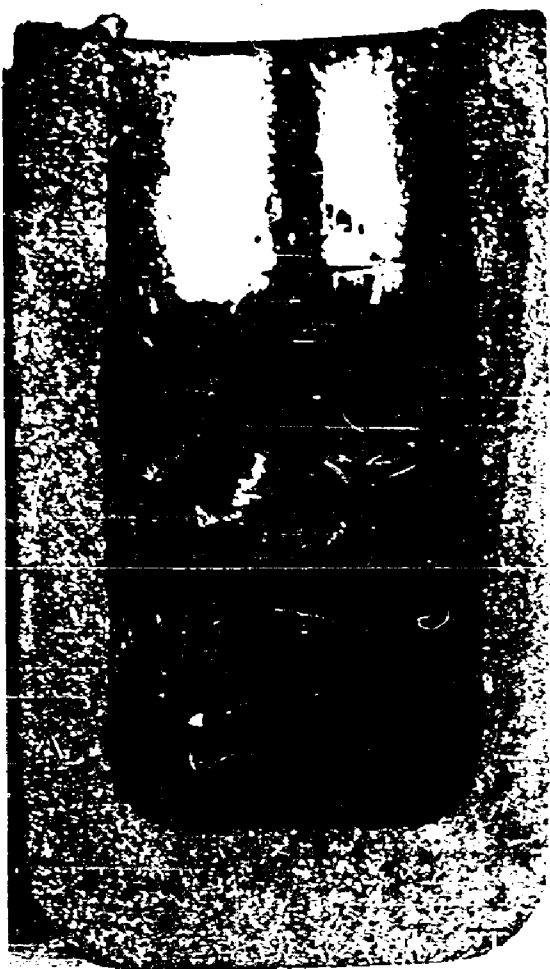


Fig. 3A - WC crucible melt showing undercutting and general solution attack by molten Ti; 2X.



Fig. 3B - TaC crucible after pouring two melts showing solution attack and metal penetration; 2X.

Fig. 3C - NbC crucible after pouring
one melt showing metal penetration;
2X.

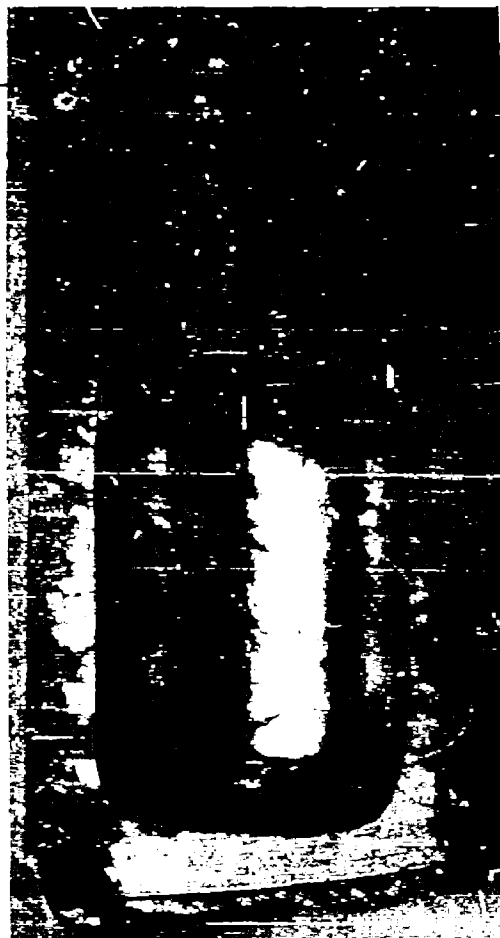


Fig. 3D - NbC crucible after pouring
two melts showing wetting and metal
penetration; 2X.



TABLE 3
Experimental Results with Carbide Crucibles

Melt No. *	Crucible Carbide	Outgas Temp.(°C)	Charge† (grams)	Melting Data			Atmos- pherest	Pourability**	Crucible Condition After Melt††
				Min. to Melt Down	Min. held Molten	Super- Heat(°C)			
RM-33-1-2	TaC	1800	18 19.5	37 98	2 10	75 100	He He	3 3	A,C A
RM-34-1-2	TiC	1700	18 18	85 102	< 1 3	< 25 25	He He	3 3	A,C A,C
RM-37-1	ZrC	1200	19.5	31	2	25	He	4	A,C
RM-39-1-2	NbC	1750	20 20	8 90	< 1 3	25 25	Vac Vac	2,3 2,3	A,C A,C
RM-40-1-2	VC	1750	20 17	15 81	1 2	25 25	Vac Vac	2,3 2,3	A,C A,C
RM-41-1-2	WC	1800	20 17	29 65	< 1 2.5	25 25	Vac Vac	2,3 2,3	A,C A,C
RM-44††	NbC		19	108	3	25	Vac	4	C
RM-46††	VC	1825	18	82	3	25	Vac	4	C
RM-49††	TiC	1850	20	90	2.5	25	Vac	4	C
RM-50††	TaC	1800	18	63	2.5	25	Vac	4	C
RM-51††	WC	1850	20	80	3.5	25	Vac	4	C
RM-55††	ZrC	1850	20	56	4	25	Vac	4	C

* Designates crucible and number of repeated melts

† Arc-fused select sponge

‡ He = pure helium (trapped); Vac = 5×10^{-6} mm Hg max

** 2 = sluggish; 3 = residual metal in crucible; 4 = solidified in crucible

†† A = attack by metal; C = wetted heavily

‡‡ Solidified in crucible

Molten titanium reacted extensively with NbC crucibles resulting in the formation of an alloy which soaked into the crucible as illustrated by Fig.3C after one melt and by Fig.3D after two melts. This tendency was also observed to occur in the case of TaC crucibles (Figs.2A and 3B).

The voids developed in all melts apparently resulted from the entrapment of a gaseous reaction product. In view of the outgassing treatment of the crucible and the use of arc-fused metal charge, the source of a gaseous product can be accounted for only as originating from a reaction involving some impurity contained in either the crucible or melt, or both.

Microscopic examination of the interface between each crucible and solidified melt revealed that reaction zones generally existed on both sides of the interface. The interfacial conditions found in the TaC crucible are shown in Fig.4A. The type of reaction which occurred at the interface in this case appeared to consist of metal penetration along carbide grain boundaries and alteration of the interface carbide by alloying. This is indicated by a narrow and indistinct zone separating carbide and melt. Corrosion of the altered carbide interface proceeded by the solvent action of molten titanium rather than by a physical mechanism.

The interfacial conditions for melts solidified in TiC crucibles were similar to those of the TaC crucibles. The conditions, illustrated by Fig.4B, consisted of a zone in the carbide which had been altered in composition by solution of Ti into TiC. ~~Since TiC can exist with a wide range of carbon content from about 6.5 to 20 wt%,~~ the carbide can be diluted with a considerable amount of Ti and still retain its phase identity. Corrosion of the altered carbide interface proceeded by the solvent action of molten titanium as was the case with the TaC crucible.

Melts made in NbC crucibles produced an interfacial reaction of slightly different pattern. In this case (Fig.5A) a new phase was apparently formed as a distinct layer between carbide and metal. The carbide phase occurring in the metallic matrix appeared to have resulted from the reaction of the melt with the intermediate layer in view of its concentration at the interface.

Titanium melts made in WC crucibles showed the development of an intermediate layer in the metal at the crucible-melt interface (Fig.5B); this zone is raised in relief showing it to be hard and probably tungsten rich. Adjacent to this zone, there was observed at 100X on the metal side another zone which appeared continuous and uninterrupted by carbides. This zone probably consists of a titanium-rich tungsten carbon alloy. The metal carbides appeared closely clustered immediately adjacent to this zone but outlined solidification grains in the interior of the melt.



Fig. 4A - Interfacial conditions existing between TaC crucible and melt; 500X, unetched, melt no. RM-50.



Fig. 4B - Interfacial conditions existing between TiC crucible and melt; 500X, unetched, melt no. RM-49.

Fig. 5A - Interfacial conditions existing between NbC crucible and melt; 500X, unetched, melt no. RM-44.

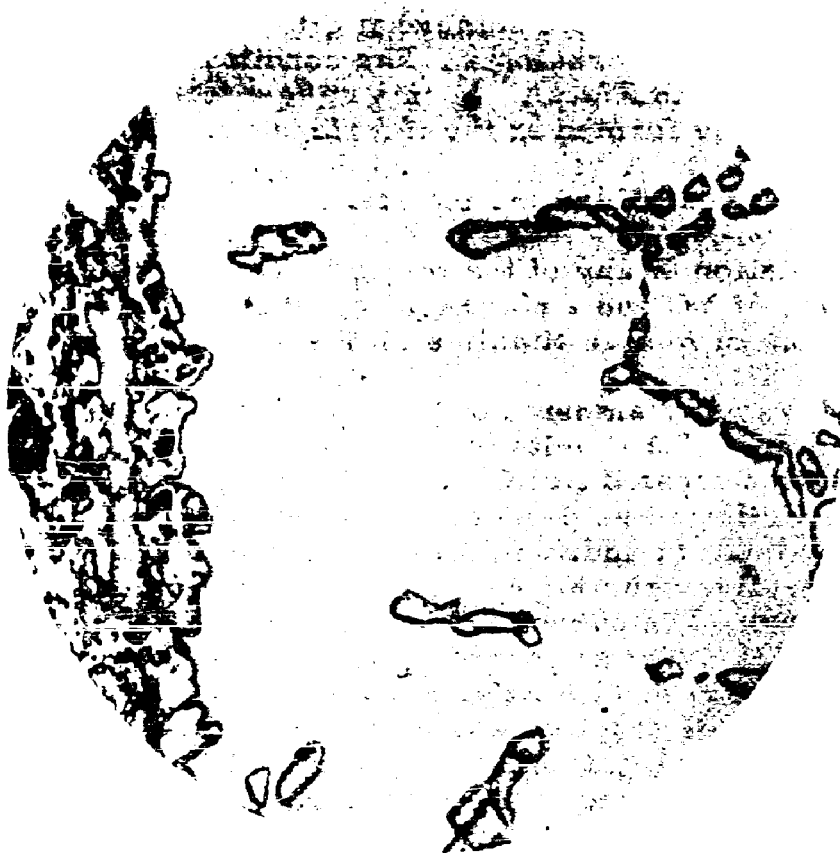


Fig. 5B - Interfacial conditions existing between a WC crucible and melt; 500X, unetched, melt no. RM-51.



Melts made in VC and ZrC crucibles showed similar interfacial characteristics but somewhat different from those observed in the other carbide crucibles. The conditions observed in a VC crucible are shown in Fig.6A. In this case a titanium-vanadium-carbon alloy apparently formed at the interface and appeared to be highly soluble in the melt. A broad zone of carbides, found adjacent to the interface, closely resembled the interface compound. A similar situation was found with melts made in ZrC crucibles (Fig.6B). The greatest contamination of any of the melts by carbon was found to occur in the cases of VC and ZrC crucibles, demonstrating the powerful solvent action of molten titanium on these crucible carbides.

Varying amounts of an insoluble residue were obtained when samples of the melts made in the various carbide crucibles were solution treated in HCl. All of the residues were found by X-ray diffraction to be predominantly titanium monocarbide (TiC) and contained, in addition, small amounts of the metallic element of the respective crucible carbide. The analytical data are summarized in Table 4. The carbon content of the TiC residues obtained from samples of metal poured from ZrC, NbC, and WC crucibles varied from 10.35 to 11.8 wt%, while that obtained from samples poured from a TiC crucible was 16.5 wt%. These values are within the carbon range established for TiC (14-16). The amounts of TiC residue, obtained from samples of the various melts, showed that the crucible carbides investigated lacked the desired chemical inertness toward molten titanium. The amount of total carbon found in the individual melts exceeded that generally considered as tolerable in titanium without adverse effects on mechanical properties. The carbon content of cast metal was generally lower than that of metal solidified in the crucible, indicating the effect of prolonged contact between crucible and melt on carbon absorption.

The oxygen content of the melts showed little or no increase over the original amount in the charge metal except in the melts made in TiC crucibles. These melts showed an increase from about 0.1 wt% initially to more than 0.2 wt% oxygen reflecting the high initial oxygen content of the TiC crucibles and the gettering power of molten titanium. Second melts poured from the crucibles generally contained less oxygen than the first melts indicating that the new crucibles contained surface oxygen which was removed by the first melt.

The microstructures of samples of melts cast from crucibles of the various carbides showed the presence of TiC in the metallic solid solution matrix as indicated by the identification of the insoluble residues. A typical example is shown in Fig.7 (a melt poured from a ZrC crucible). Since no free carbon was found in the respective crucible carbides, it is concluded that titanium has a stronger affinity for carbon than the elements Zr, V, Nb, Ta, or W and is capable of reducing the carbides of these elements at the interface to form TiC. This appears to agree with that predicted from the free energy of formation values listed in Table 1, of which TiC has the highest value.

Fig. 6A - Interfacial conditions existing between VC crucible and melt; 100X, unetched, melt no. RM-46.

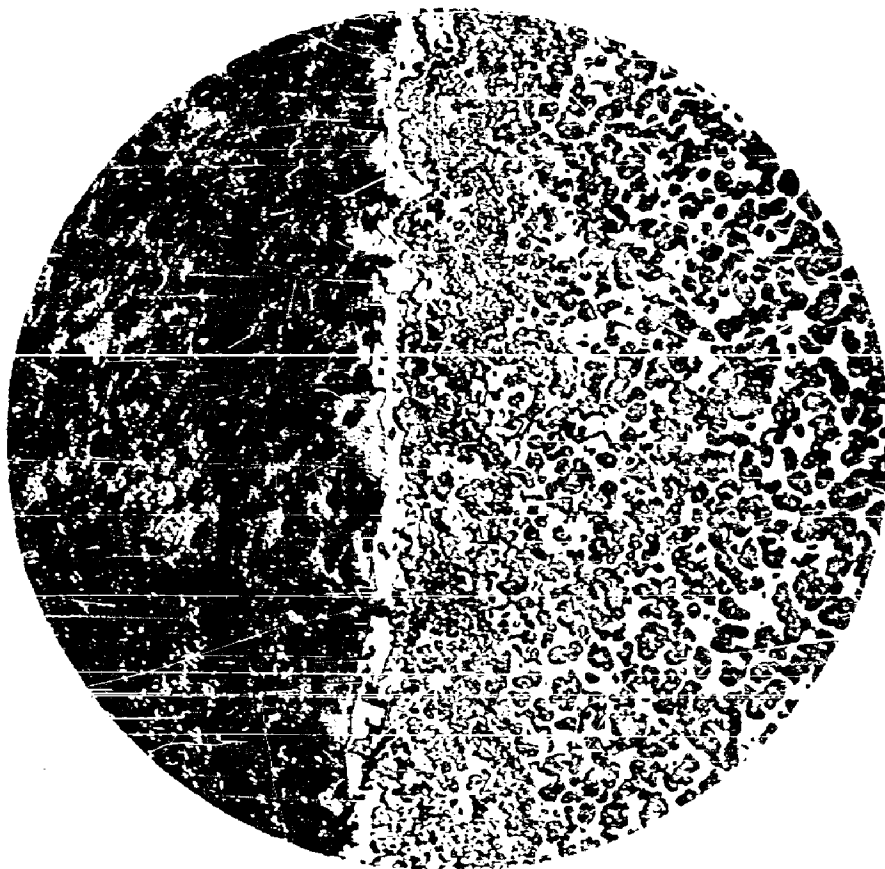
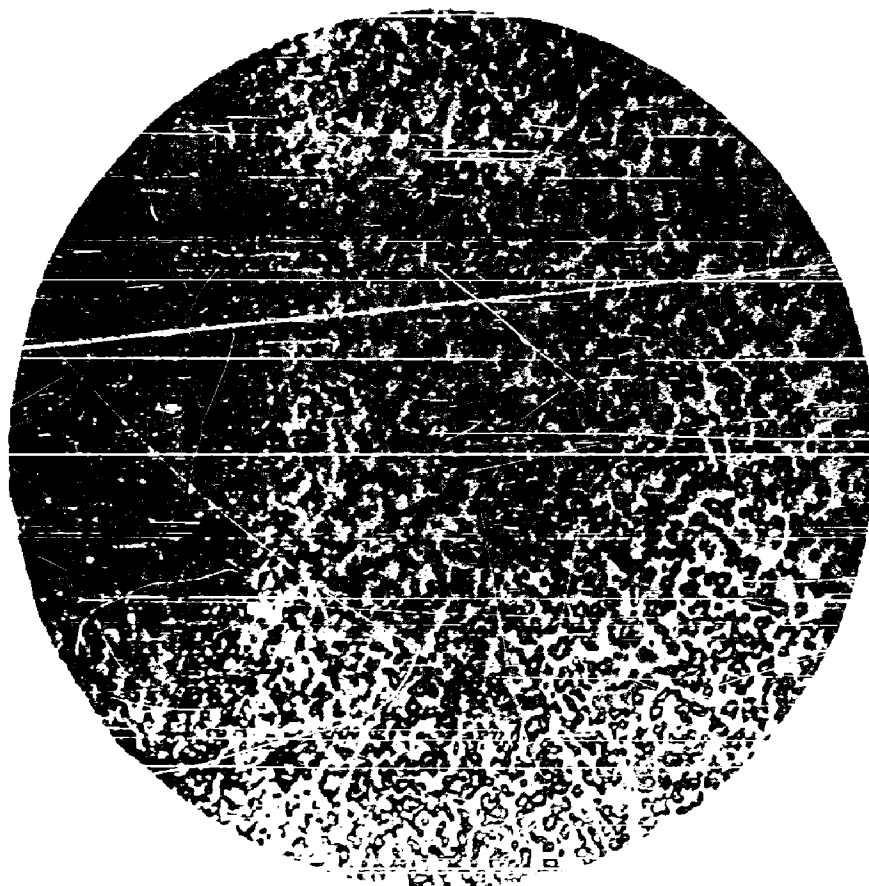


Fig. 6B - Interfacial conditions existing between ZrC crucible and melt; 100X, unetched, melt no. RM-55.



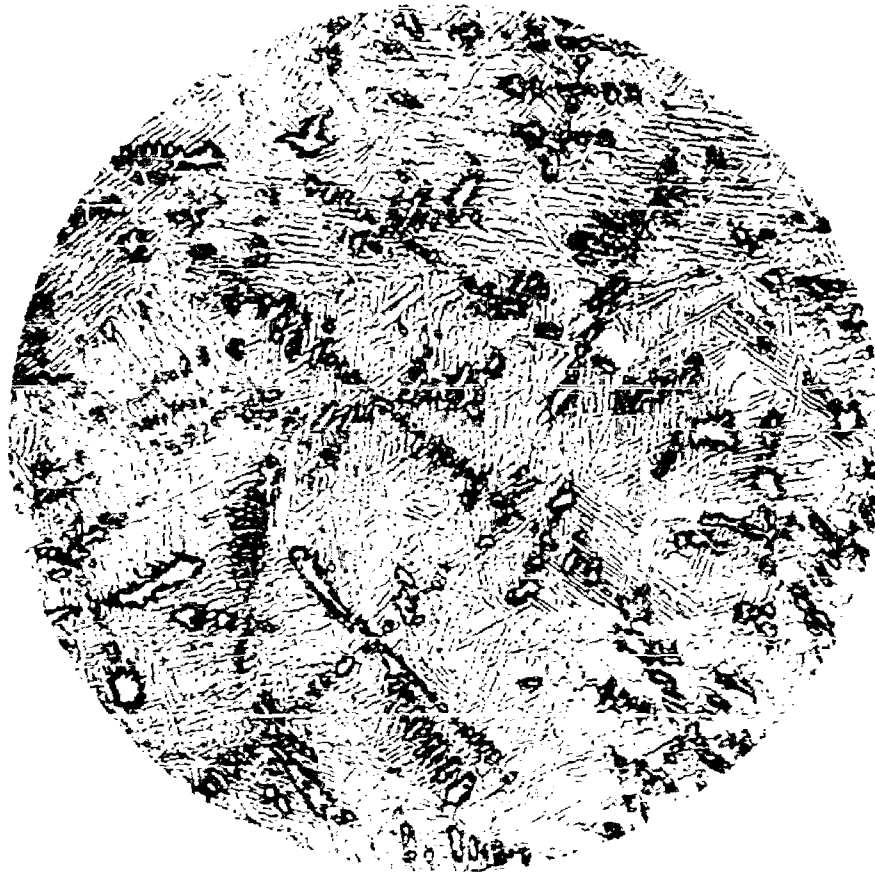


Fig. 7 - Typical microstructure of melts made in carbide crucibles, showing titanium carbides in the solid solution metallic matrix; 100X, etched, melt no. RM-37-1.

A review of the hardness values obtained on samples of the various melts (Table 4) showed a range from about 231 to 314 DPH for cast metal and from 215 to 459 DPH for metal solidified in the crucible. Second melts cast from the various crucibles showed lower carbon contents and correspondingly lower hardnesses than the first melts. It would appear from this trend that the formation of an interface layer during the first melt retarded slightly the carbon absorption into the second melt. The reverse occurred in the case of TiC where the carbon content and corresponding hardness increased in the second melt.

On the basis of data shown in Table 4 it is not possible to select a single crucible carbide which displays some particular advantage over the others or which shows superior resistance to molten titanium. Titanium appeared to attack, in varying degree, all of the crucible carbides investigated. Most of the metallic elements of the crucible carbides are extensively soluble in titanium so that the reaction at the interface between molten metal and the crucible carbide resulted generally in a titanium-rich solid solution of carbon and the metallic element of the respective crucible carbide plus the TiC carbide phase. The difficulty experienced in pouring the melts indicated that the melting point was increased by the solution of the interface reaction products into the melt. Thus, to obtain a desirable melt fluidity, a high superheat is required which in turn increases reactivity of the molten metal and of the crucible carbide, accelerating the attack on the crucible. Such a process would result in contamination of the metal with carbon beyond any acceptable limit.

The carbide crucibles investigated were of excellent quality and it is believed that the impurity content was insufficient to materially affect the results obtained. All of the carbide crucibles investigated were insufficiently resistant to molten titanium to be recommended as suitable crucible materials.

SUMMARY

Crucibles of high-purity carbon and graphite were investigated to determine if purity was a beneficial factor for melting titanium. Pure carbon crucibles were cast in glass molds from a furfural-acid reaction. The resulting carbon surfaces after firing and outgassing were dense, highly smooth, and tight. Titanium melted in this type of material absorbed about 3.5 wt% carbon from which it may be concluded that no benefits were obtained from either the special surfaces or the high purity of the carbon.

Commercially pure and spectroscopically pure graphite crucibles were found to be unsatisfactory. Molten titanium soaked entirely through the commercially pure graphite crucibles, while partial soaking occurred in the spectroscopically pure graphite crucibles. Metal from these crucibles showed carbon contamination similar in character and amount to that from the carbon crucibles.

TABLE 4
Chemical Analyses and Hardnesses of Samples of Melts made in Carbide Crucibles

Melt No. *	Crucible Carbide	Insoluble Residue in HCl			Total Carbon (%)	Oxygen (%)	Hardness (DPH)	
		Percent	Identity	Principal Impurity			As Cast	Solidified in Crucible
RM-33-1-2	TaC	1.01	TiC	Ta	1.21 0.96	0.078 0.050	284 266	
RM-34-1-2	TiC	10.4 12.94	TiC TiC		16.5	0.208 0.151	249† 275	
RM-37-1	ZrC	12.10† 11.67**	TiC	Zr Zr	12.0† 11.0**	0.103	252	
RM-39-1-2	NbC	8.96 10.92	TiC TiC	Nb Nb	11.8	0.092 0.092	221† 231	
RM-40-1-2	VC	3.42 7.40	TiC TiC	N	1.12	0.106	240	
RM-41-1-2	WC	12.95 9.68	TiC TiC	V W W	0.96 1.62 0.74	0.092 0.137 0.102	248 282 273	
RM-44††	NbC		TiC		0.63			246††
RM-46††	VC		TiC		3.77			280† 245**
RM-50††	TaC	6.35	TiC	Ta	1.10			215††
RM-51††	WC	7.84	TiC	W	1.49			459† 394**
RM-55††	ZrC		TiC		3.26			345† 251**

* Designates crucible and number of repeated melts

† Annealed 1000°C

‡ Inside interfacial zone of melt

** Interior of melt

†† Solidified in crucible

‡‡ Average across entire cross section

A TiC interface layer, formed in both the carbon and graphite crucibles, was not effective in preventing the contamination of the melt with carbon. This carbon absorption developed hardnesses beyond an amount considered acceptable for good metal quality.

The monocarbides of Ti, Zr, V, Nb, Ta, and W were investigated to determine their suitability as crucible materials for melting titanium. The quality of these carbide crucibles was excellent and the impurity content was believed to be insufficient to affect the results obtained. Even though these materials exhibited good thermal shock resistance, good strength, and nonvolatility at high temperatures, all the carbides were attacked and wetted by molten titanium resulting in general solution of the crucibles and in severe contamination of the melt with carbon. Although the microstructures of samples of the various melts contained appreciable amounts of the TiC phase, hardnesses were not unduly high, ranging from about 231 to 314 DPH.

The reaction at the liquid-solid interface between molten titanium and the various crucible carbides resulted in their reduction with the formation of titanium monocarbide (TiC) in each case. This is in agreement with thermodynamic data which indicates that Ti has a higher affinity for carbon than the elements Zr, V, Nb, Ta, or W.

Difficulty was experienced in pouring the melts. This is believed to have been caused by an increase in melting point resulting from the solution of the reaction products produced at the interface. In order to obtain a fluid melt an increased temperature is required which increases the reactivity and thereby results in an increased contamination of the melt. Thus, under such circumstances it would not be possible to melt titanium in carbide crucibles and preserve the metal quality. It is therefore concluded that the carbides cannot be recommended as suitable crucible materials.

* * *

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